High-Temperature Stability of δ' -ZrO

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Abstract

We investigate phase stability in the Zr-O system from first principles, focusing in particular on the finite temperature stability of the newly discovered δ' -ZrO phase. We present a first-principles phase diagram of the Zr-O binary that accounts for both configurational and vibrational excitations. Phonon calculations within the quasi-harmonic approximation predict that δ' -ZrO is stable to at least 1500 K. Quasi-harmonic phonon calculations also predict an α - to β -ZrO₂ transition temperature of 1440 K. Stiff Zr-O bonds are responsible for a low vibrational entropy in the δ' -ZrO phase compared to competing oxides in the Zr-O binary, resulting in a reduction in its stability relative to ZrO_{1/2} and ZrO₂ with increasing temperature. The calculated thermodynamic properties are relevant to understanding oxidation mechanisms of Zr-based alloys.

Keywords: Zirconium; First-principles calculations; Phase Diagram

1. Introduction

The oxidation of zirconium alloys has long been of interest as it is an important degradation mechanism of nuclear fuel-rod cladding in water-based reactors. The harsh reactor environments induce waterside corrosion of the Zr-alloy cladding. An experimental understanding of the resulting oxide microstructures is especially important to designing alloys with greater corrosion resistance [1, 2, 3]. Computational efforts can provide further insight into the thermodynamic driving forces behind these complex oxidation processes, which are determined by the relative stabilities of various oxides at high temperatures. While zirconium alloys have been extensively studied, resulting in both experimental [4, 5] and computational phase diagrams [6, 7], new discoveries of the material continue to emerge.

A notable characteristic of the Zr-O phase diagram is the extraordinary oxygen solubility in α -Zr, reported to reach values up to 35 at.% [5]. Various sub-oxide phases are formed at low-temperatures in which oxygen orders over the interstitial sites of α -Zr [8, 9, 10]. At higher temperatures these suboxides disorder and form an α Zr-O solid-solution. Calculated phase diagrams [6, 7, 5] show an ordered suboxide having ZrO_{1/2} stoichiometry, which is close to the oxygen solubility limit. The tolerance for vacancies on the oxygen sublattice of this ordered suboxide is predicted to increase with temperature. The well-studied ZrO₂ polymorphs form at higher oxygen concentrations [8, 9, 10]. Monoclinic α -ZrO₂ is stable up to 1478

K, upon which it transforms to tetragonal β -ZrO₂ [4]. A non-stoichiometric cubic γ -ZrO₂ becomes stable [5] above approximately 1800 K. The oxide scales of Zr often contain several oxide phases. The formation of these oxides as a function of distance from the oxidation surface is a result of an oxygen chemical potential gradient that exists between the exterior surface, where the oxygen chemical potential is high, and the interior unexposed regions of the nuclear cladding material, where the oxygen chemical potential is low [7].

Recently, a monoxide ZrO phase was discovered experimentally via EELS, atom probe tomography, and electron diffraction [8, 9, 11]. Its hexagonal structure was determined with first-principles methods [7] and subsequently confirmed experimentally [11]. This phase was previously identified as a line compound, labeled as δ' -ZrO, in a first-principles calculated phase diagram [7], but as only configurational entropy had been considered, its finite temperature stability limits remain unknown. Determining the stability of δ' -ZrO relative to ZrO_{1/2} and ZrO₂ at elevated temperatures is important due to the high-temperature environments under which nuclear rod claddings are subjected.

Here we examine the stability of Zr-O phases at the nuclear cladding operating temperatures of 300-360° C from first principles by calculating vibrational free energies within the quasi-harmonic approximation. We calculated temperature and volume-dependent free energies of α -Zr, ZrO_{1/2}, δ' -ZrO, α -ZrO₂ and β -ZrO₂ within the quasi-harmonic approximation and determined that δ' -ZrO is stable to at least as high as 1500 K. Nevertheless, our calculations predict that the oxygen chemical potential window in which δ' -ZrO is stable decreases with increasing

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temperature due to its lower vibrational entropy relative to that of competing oxides in the Zr-O binary. We also report a prediction of the α to β ZrO₂ transition temperature of 1440 K. With the calculated vibrational free energies, adjustments were made to the phase diagram in Reference [7] to include the contribution of finite temperature vibrational effects.

2. Methodology

The Zr-O temperature composition phase diagram was previously calculated using first-principles cluster expansion Hamiltonians and Monte Carlo calculations [6, 7]. While rigorously accounting for configurational degrees of freedom due to oxygen-vacancy disorder over the interstitial sites of hcp Zr, these studies neglected the role of vibrational excitations. Here we build on the phase diagram of [7] by calculating vibrational free energies of key compounds in the Zr-O binary. We are primarily interested in the stability of the newly discovered δ' -ZrO phase at elevated temperature. Whether or not δ' -ZrO remains stable at high temperature depends on the value of its free energy relative to those of ZrO_{1/2} and ZrO₂.

The temperature dependence of the free energies of δ' -ZrO as well as those of α and β -ZrO₂ are primarily determined by vibrational excitations since these phases are line compounds with negligible configurational disorder [7, 5]. While ZrO_{1/2} corresponds to an ordered phase, Monte Carlo simulations [6, 7] have shown that it can tolerate some disorder and oxygen off-stoichiometry at high temperature. Hence the temperature dependence of its free energy has contributions from both vibrational and configurational excitations. Although the coupling between configurational and vibrational excitations can be treated rigorously using coarse graining techniques [12], these approaches are computationally prohibitive. Here we estimate the free energy of ZrO_{1/2} by approximating it as a sum of a configurational free energy $G_{\text{config}}(x, T)$ and a vibrational free energy $G_{\text{vib}}(x, T)$. We further assume that the dependence of the vibrational free energy on concentration in HCP based α ZrO_x can be linearly interpolated between that of α Zr and ordered ZrO_{1/2} [12]. These approximations should be reasonable for the purpose of calculating the stability of δ' ZrO relative to ZrO_{1/2} and ZrO₂. While ZrO_{1/2} can tolerate a high degree of oxygen off-stoichiometry at elevated temperature, its concentration when in equilibrium with more oxygen rich oxides (i.e. ZrO or ZrO₂) remains very close to that of the stoichiometric compound.

To obtain the vibrational Gibbs free energies, G_{vib} , force constants are needed to construct a lattice dynamics model within the harmonic approximation. The frozen phonon approach was used to calculate force constants for each of the phases. Single atom perturbations were applied in high symmetry directions in large supercells. Forces resulting from these perturbations were obtained through

high precision calculations using the Vienna Ab Initio Simulation Package (VASP) [13, 14]. A least squares fit between the displacements and forces was performed to extract force constants that were then used in the construction of the dynamical matrix [15, 16, 17, 18, 19]. First-principles calculations of forces were performed within the generalized gradient approximation (GGA) to density functional theory using the PBEsol parameterization [20]. This parameterization has been shown to be superior to other parameterizations in predicting lattice parameters and phonon properties for ZrO₂ [21]. A 600 eV energy cutoff was used for the plane wave basis. Projector augmented wave [14, 22] pseudopotentials were used having valence-electron configurations of $4s^2, 4p^6, 5s^1, 4d^3$ and $2s^2, 2p^4$ for Zr and O, respectively.

As both α and β forms of ZrO₂ are insulating materials, contributions from long wave length dipole-dipole interactions must be accounted for [23, 24, 25, 26]. These dipole-dipole interactions are not present in either ZrO_{1/2} or δ' -ZrO as they are both metallic [7]. The non-analytical contribution to the dynamical matrix resulting from long-range dipole-dipole interactions was calculated according to the interpolation scheme of Parlinski et al [27]. Born effective charges and dielectric tensors were calculated with a linear response approximation [25] as implemented in VASP [28].

Vibrational free energies within the quasi-harmonic approximation were calculated for Zr, ZrO_{1/2}, δ' -ZrO, α -ZrO₂, and β -ZrO₂ by performing harmonic phonon calculations at varying volumes. At each volume, displacements of 0.03 Å were imposed in the $3 \times 3 \times 2$ (36 atoms), $2 \times 2 \times 4$ (96 atoms), $2 \times 2 \times 2$ (72 atoms), and $3 \times 3 \times 3$ (324 atoms) supercells of Zr, ZrO, ZrO_{1/2}, and α -ZrO₂, respectively. Amplitudes of 0.048 and 0.037 Å were imposed on the O and Zr atoms, respectively, in a $3 \times 3 \times 2$ (108 atoms) supercell of β -ZrO₂. A Monkhorst-Pack [29] k -point mesh of $4 \times 4 \times 4$, $5 \times 5 \times 4$, $7 \times 7 \times 7$, $3 \times 3 \times 3$, and $5 \times 5 \times 5$ was used for each supercell of Zr, ZrO, ZrO_{1/2}, α -ZrO₂, and β -ZrO₂ when calculating forces with VASP using DFT-PBEsol. The Gibbs free energy as a function of temperature was calculated by minimizing each iso-thermal, volume-dependent free energy curve via a second order polynomial fit.

3. Results

Experimentally, the oxidation of zirconium alloys manifests itself as a sequence of ZrO_x suboxides, a monoxide, and ZrO₂ [8, 9]. Of the ZrO_x suboxides, the ordered phase with the widest region of stability both as a function of oxygen concentration and temperature is ZrO_{1/2}. The crystal structures of ZrO_{1/2} and ZrO₂ are well-known. The crystal structure of ZrO_{1/2} (Figure 1a) consists of an HCP Zr sublattice with oxygen atoms occupying octahedral sites between the triangular close-packed Zr-layers. The other ordered ZrO_x suboxides share the same HCP Zr

sublattice with varying oxygen occupation. ZrO_2 forms on the surface of the oxidizing metal due to the high oxygen chemical potential there. In this region, two of the three polymorphs are often observed. One is tetragonal $\beta\text{-ZrO}_2$, shown in Figure 1b, which has O atoms occupying tetrahedral interstitial sites of the tetragonally distorted FCC Zr sublattice, forming an 8-fold coordination around Zr. The Zr in the low-temperature monoclinic $\alpha\text{-ZrO}_2$ polymorph, shown in Figure 1c, is 7-fold coordinated by oxygen. While the connectivity of Zr in both α and $\beta\text{-ZrO}_2$ is that of FCC, in $\alpha\text{-ZrO}_2$, it is highly distorted.

The newly identified $\delta'\text{-ZrO}$ monoxide phase has hexagonal symmetry with a Zr sublattice identical to $\omega\text{-Zr}$. It consists of two distinct layers each denoted by a different shade of green in Figure 1d. The first layer is a triangular Zr sublattice while the second layer is a honeycomb Zr sublattice, each outlined with a red and blue dashed line, respectively. Each Zr atom of the triangular sublattice is situated directly above and below the center of each honeycomb. The oxygen are coordinated by 5 Zr atoms, forming a square pyramidal polyhedron, where the O atom is not quite coplanar with the square base of Zr atoms. The purple dashed line in Figure 1e shows the outline of this pyramid. The square base of the pyramid is composed of four atoms from the honeycomb layer, while the tip of the pyramid belongs to the triangular sublattice. The O-Zr bond formed with the apex of the square pyramid is 2.15 Å, shorter than the 2.26 Å bonds formed with the pyramid base. The compact pyramidal coordination of oxygen by Zr suggests that oxygen in $\delta'\text{-ZrO}$ is tightly bound, which will have implications for the shape of the dispersion curve and density of states.

The phonon dispersion curve and corresponding density of states of $\delta'\text{-ZrO}$ are shown in Figures 2 and 3. The most notable feature of the dispersion curve is the vibrational bandgap. The partial density of states (Figure 3) shows that the majority of the optical vibrational modes above the gap are dominated by oxygen while the acoustic modes are dominated by Zr. The high oxygen vibrational frequencies suggests that the oxygen are strongly bound within the tight pyramidal coordination geometry of the Zr sublattice. The large separation in vibrational frequencies also arises in part from a large mass difference, with Zr being about 5.7 times heavier than O.

The partial densities of states for neighboring phases $\text{ZrO}_{1/2}$ and $\alpha\text{-ZrO}_2$ are also shown in Figure 3, and their dispersion curves are provided in Supplementary Materials. Similar to $\delta'\text{-ZrO}$, Figure 3a shows that the oxygen frequencies are well separated from the Zr frequencies in $\text{ZrO}_{1/2}$. Compared to $\text{ZrO}_{1/2}$, both the oxygen and zirconium frequencies of $\delta'\text{-ZrO}$ are shifted up. This behavior indicates an overall increase in bond stiffness in $\delta'\text{-ZrO}$ relative to $\text{ZrO}_{1/2}$. In $\alpha\text{-ZrO}_2$ the O and Zr vibrational frequencies are more evenly distributed. Nevertheless, the majority of the acoustic modes are still dominated by Zr. While some vibrational modes have high frequencies the absence of a vibrational band gap in $\alpha\text{-ZrO}_2$ ensures that

Figure 1: Crystal structures of (a) $\text{ZrO}_{1/2}$ (b) $\beta\text{-ZrO}_2$ (c) $\alpha\text{-ZrO}_2$ and (d) $\delta'\text{-ZrO}$. The $\delta'\text{-ZrO}$ oxygen interstitial sites, shown as red squares, and coordination with neighboring Zr are shown in (e). Green and red atoms represent Zr and O, respectively. Different shades of green and red in (a), (d), and (e) differentiate atoms on different layers of the crystal. The triangular and honeycomb sublattices in ZrO are shown in red and blue dashed lines. Different layers of the triangular sublattices of $\text{ZrO}_{1/2}$ are also shown in red and blue dashed lines.

Figure 2: Dispersion curve of $\delta'\text{-ZrO}$ showing a vibrational band gap.

Figure 3: (a) Oxygen and (b) zirconium vibrational partial density of states of $\text{ZrO}_{1/2}$, δ' -ZrO, and α -ZrO₂. The total density of states is shown by a black outline. For $\text{ZrO}_{1/2}$ and δ' -ZrO, there is a clear distribution of oxygen and zirconium vibrational states between high and low frequencies.

a large fraction of modes dominated by oxygen occur at frequencies below the oxygen vibrational frequencies in $\text{ZrO}_{1/2}$ and δ' -ZrO.

A quasi-harmonic analysis was performed to obtain Gibbs free energy curves of several ordered Zr-O phases. Figure 4 shows calculated Helmholtz vibrational free energies as a function of volume. By minimizing the isothermal Helmholtz free energies, we obtain G_{vib} at zero pressure for each of the 5 ordered phases. These free energies are superior to those from the harmonic approximation in that finite temperature volume expansion is included in the quasi-harmonic approximation. Figure 5 shows both the configurational entropy and the vibrational entropy as a function of oxygen concentration. The configurational entropy was determined by subtracting the internal energy

from the free energy, both calculated with Monte Carlo simulations applied to a cluster expansion for the HCP based ZrO_x phase [7]. Minima in the configurational entropy indicate the presence of an ordered phase, the most prominent of which is $\text{ZrO}_{1/2}$. The black line denotes the ideal solution entropy multiplied by the temperature at 1200 K. As the ideal solution entropy corresponds to the maximum configurational entropy, it is always higher than the configurational entropy of a solid with interacting atoms exhibiting some degree of short- or long-range ordering. As is clear from Fig. 5, the vibrational entropy is substantially larger than the configurational entropy. The vibrational entropy per Zr of $\text{ZrO}_{1/2}$ is also larger than that of α Zr, which is consistent with the introduction of more vibrational degrees of freedom upon insertion of oxygen.

At finite temperatures, vibrational entropy begins to play a role in the relative stabilities of phases. The effect on $\text{ZrO}_{1/2}$ and δ' -ZrO at elevated temperatures, for example, can be seen in Figure 7, where the formation vibrational entropies (per Zr) for both phases relative to α -Zr and α -ZrO₂ are shown. The formation entropies for both phases are negative. Hence the formation of either $\text{ZrO}_{1/2}$ or δ' -ZrO from a two phase mixture of Zr and ZrO₂ is accompanied by a reduction in vibrational entropy. The formation vibrational entropy per Zr of δ' -ZrO is even more negative than that of $\text{ZrO}_{1/2}$, indicating that with increases in temperature, vibrational entropy stabilizes δ' -ZrO to a lesser extent than it does $\text{ZrO}_{1/2}$. This is consistent with the vibrational densities of state of Figure 3, which shows that the bonds are stiffer in δ' -ZrO than in $\text{ZrO}_{1/2}$.

To incorporate vibrational effects into the phase diagram, we approximated the total free energy G_{total} as a sum of separate configurational G_{config} and vibrational G_{vib} components. Representative total free energies are shown in Figure 6. The vibrational entropy (Figure 5) results in a lowering of the free energy with increasing temperature. Application of the common tangent construction at each temperature yields the phase boundaries shown in the phase diagram of Figure 8, which now includes both configurational and vibrational entropy. The most notable change to the phase diagram is that δ' -ZrO is now stable to at least 1500 K. The entropic stabilization of $\text{ZrO}_{1/2}$ relative to δ' -ZrO (Figure 7) translates into an increase in the oxygen solubility limit of the $\text{ZrO}_{1/2}$ phase. The dashed line in the $\text{ZrO}_{1/2}$ region of the updated phase diagram denotes the original two-phase boundary as calculated when only considering configurational degrees of freedom. This boundary shifts towards higher oxygen concentrations with the inclusion of vibrational entropy. The monoclinic α -ZrO₂ forms at higher oxygen concentrations and is predicted to be stable until 1440 K after which it transforms to tetragonal β -ZrO₂. This temperature is in good agreement with the experimental transition temperature of 1478 K [4].

The relative stability of the various oxides in the Zr-O

Figure 4: Quasi-harmonic volume-dependent free energy curves for (a) δ' -ZrO, (b) $\text{ZrO}_{1/2}$, (c) α -ZrO₂, (d) β -ZrO₂, and (e) α -Zr. Curves are shown at increments of 100 K between 0 - 1500 K. The Gibbs free energy obtained by minimizing each isothermal curve was incorporated into the phase diagram in Figure 8 to account for finite temperature effects.

Figure 5: Vibrational TS^{vib} (a) and configurational TS^{config} (b) entropies as a function of composition. The black line denotes the ideal solution entropy at 1200 K.

Figure 6: Total Gibbs free energy, including both vibrational and configurational contributions, at various temperatures.

Figure 7: Formation vibrational entropy of both δ' -ZrO and $\text{ZrO}_{1/2}$ relative to α -Zr and α -ZrO₂, calculated as $\Delta S_{\delta'\text{-ZrO}} = S_{\delta'\text{-ZrO}} - 1/2 S_{\text{ZrO}_2} - 1/2 S_{\text{Zr}}$ and $\Delta S_{\text{ZrO}_{1/2}} = 1/4 S_{\text{ZrO}_2} + 3/4 S_{\text{Zr}}$. δ' -ZrO is less entropically stabilized at finite temperatures than $\text{ZrO}_{1/2}$.

binary becomes apparent upon inspection of the variation of the oxygen chemical potential with oxygen concentration. Calculated oxygen chemical potentials at 300 and 600 K are shown in Figure 9. These are related to the slopes of the Gibbs free energies in Figure 6 with respect to the oxygen concentration x . Steps in a chemical potential versus concentration plot correspond to stoichiometric compounds, while solid solutions appear as sloping regions. Plateaus signify two-phase regions since the chemical potentials of coexisting phases remain constant in equilibrium. Figure 9 shows that the collection of HCP based ZrO_x suboxides as well as α ZrO_2 are stable in wide oxygen chemical potential intervals. δ' -ZrO, however, is stable in only a narrow chemical potential window. Furthermore, the stability window of δ' -ZrO decreases with increasing temperature.

4. Discussion

Our first-principles calculation of the vibrational free energies of compounds in the Zr-O binary predicts that the newly discovered δ' -ZrO remains thermodynamically stable to temperatures above 1500 K. The updated phase diagram of Figure 8 now accounts for both configurational [7] and vibrational degrees of freedom. The phase diagram below $x < 1/2$ remains unaffected by our inclusion of vibrational contributions since we approximated the vibrational free energy between $x = 0$ and $x = 1/2$ as a linear interpolation between the vibrational free energies of α Zr and ordered $\text{ZrO}_{1/2}$. Adding a linear term to a free energy curve as a function of concentration does not affect the common tangent construction and will therefore not alter phase boundaries or order-disorder transition temperatures. Since the crystal structure and lattice parameters of HCP based ZrO_x vary negligibly with oxygen concentration [7] we do not expect that a more rigorous inclusion of

vibrational degrees of freedom using for example a coarse graining scheme [12] will alter the topology of the phase diagram below $x = 1/2$ much. Inclusion of vibrational contributions does, however, increase the oxygen solubility limit of ordered $\text{ZrO}_{1/2}$ when it coexists with δ' -ZrO. This is due to the low vibrational entropy within δ' -ZrO compared to $\text{ZrO}_{1/2}$ and the α and β polymorphs of ZrO_2 . Oxygen within the Zr_5O square pyramidal interstitial sites of the ω -Zr sublattice of δ' -ZrO are tightly bound resulting in high frequency optical modes.

As is evident from the updated phase diagram in Figure 8, the concentration of ordered $\text{ZrO}_{1/2}$ when it coexists with δ' -ZrO is close to ideal stoichiometry. Hence, our linear interpolation scheme to approximate the vibrational free energy of HCP based ZrO_x should be sufficiently accurate for the purposes of assessing the stability of δ' -ZrO relative to $\text{ZrO}_{1/2}$ and ZrO_2 at elevated temperature.

The calculated phase diagram of Figure 8 shows fair agreement with a previously published phase diagram (between 0 – 1500 K) as assessed with the CALPHAD approach [5]. The ordered HCP-based phases, $\text{ZrO}_{1/6}$, $\text{ZrO}_{1/3}$, and $\text{ZrO}_{1/2}$, appear in both phase diagrams, although $\text{ZrO}_{1/2}$ in Figure 8 is predicted to be stable to much higher temperatures [7]. The primary difference between the two phase diagrams is the presence of the recently identified δ' -ZrO line compound.

The relative stability between α and β - ZrO_2 has been investigated before within the harmonic [30] and quasi-harmonic approximation [31]. While the quasi-harmonic study [31] did not include the effect of long-range dipole-dipole interactions, our calculated vibrational free energies do account for such effects, as did the previous harmonic study [30]. Furthermore, in contrast to prior treatments [31], our harmonic Hamiltonians for α - ZrO_2 did not predict spurious unstable modes (i.e. imaginary frequencies). We believe this is due to our use of significantly larger supercells to extract force constants (324 compared to 108 in a previous study [31]), which have allowed for longer-range force constants to be included in the harmonic Hamiltonian, as Kuwabara et al suspected [31].

Experimental observations [9] of Zr metal-oxide interfaces oxidized at temperatures of 360° C (633 K) have shown narrow regions of ZrO wedged between ZrO_2 and HCP based ZrO_x suboxides (with $x < 1/2$). Zr samples exposed to air will have a gradient in oxygen chemical potential that is high at the surface and that decreases monotonically towards the interior of the sample. While kinetic factors play a role in determining the presence and distribution of different oxide phases in an oxidizing microstructure, the thickness of a particular oxide phase in a monotonically decreasing oxygen chemical potential profile should to a large extent depend on the width of oxygen chemical potential window in which the phase is thermodynamically stable. As is clear from Figure 9, δ' -ZrO at $x=1$ is only stable in a very narrow oxygen chemical potential window. This is consistent with experimental observations that δ' -ZrO appears as much thinner regions

Figure 8: Updated Zr-O phase diagram including contributions from both configurational and vibrational excitations. Compared to the original Zr-O phase diagram [7], δ' -ZrO is now shown to be stable to at least 1500 K. Single-phase regions are shaded in, while two-phase regions are left white. The boundary between $\text{ZrO}_{1/2}$ and the neighboring two-phase region based solely on configurational and excluding vibrational free energies is denoted by a dashed line. The oxygen solubility of oxygen in $\text{ZrO}_{1/2}$ increases when contributions from vibrational excitations are also included.

compared to ZrO_2 and the collection of HCP based ZrO_x suboxides. Figure 9 also shows that the chemical potential stability window of δ' -ZrO decreases with increasing temperature. This suggests that the relative thickness of the δ' -ZrO phase in oxidizing samples will decrease as the temperature is raised. The diminishing relative stability of δ' -ZrO with increasing temperature is a result of its lower vibrational entropy compared to $\text{ZrO}_{1/2}$ and ZrO_2 .

While our calculation of thermodynamic properties predict that δ' -ZrO remains stable to high temperatures, it does not shed light on the role of this phase in affecting the kinetics of Zr oxidation. Important in this regard is whether the interfaces between the various oxides tend to be coherent, semicoherent or incoherent. The crystallographic nature of the interface will determine how mobile the interface is between a pair of oxides as oxidation proceeds. Another important factor is the oxygen mobility through the different phases. Although oxygen diffusion coefficients in the HCP based ZrO_x suboxides have been predicted to be high at elevated temperature [32], oxygen mobility in the more compact crystal structures of δ' -ZrO will likely be low. δ' -ZrO may therefore act as a diffusion barrier, slowing oxygen ingress in the HCP metal substrate. If so, then it will be desirable to devise strategies that result in a thick δ' -ZrO phase within the oxidizing microstructure. Alloying would have to aim at increasing the energetic stability δ' -ZrO relative to $\text{ZrO}_{1/2}$ and ZrO_2 since our current study suggests there is little maneuverability to enhance finite temperature entropic stabilization of the phase.

Figure 9: Oxygen chemical potential at different temperatures. Single-phase regions have increasing μ_O , while two-phase regions have constant μ_O .

5. Conclusion

The primary aim of this study was to determine the finite temperature phase stability of the newly discovered δ' -ZrO phase relative to other oxides in the Zr-O binary. Vibrational free energies calculated within the quasi-harmonic approximation were combined with free energies accounting for configurational degrees of freedom to construct a Zr-O composition-temperature phase diagram. The calculated phase diagram shows that δ' -ZrO is stable to at least 1500 K. Phonon dispersion curves and corresponding partial density of states reveal that the O and Zr atoms are tightly bound in δ' -ZrO. This results in a lower vibrational entropy for δ' -ZrO relative to that of $\text{ZrO}_{1/2}$ and ZrO_2 , causing a reduction in the stability of δ' -ZrO with increasing temperature. We also calculated an α - β -ZrO₂ transition temperature of 1440 K.

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